

Amendments to the Specification

Please make the following amendments to the specification. Changes relative to the immediate prior version are shown using strikethrough to identify deleted material and underlining to identify added material, except that when strikethrough would be difficult to perceive (e.g., as in the deletion of punctuation marks, such as hyphens, and the numeral 9), double brackets are used instead of strikethrough to identify the deleted material.

Please replace paragraph 0098 on page 14 with the following amended paragraph:

– For further description of hydrogen-bond promoted acceleration of ~~HAD~~ HDA reactions in accordance with the present invention, see: Huang, Y.; Viresh, V. H. *J. Am. Chem. Soc.*, **2002**, *124*, 9662-9663, the entire contents of which are incorporated herein by reference, except that in the event of any inconsistent disclosure or definition from the present application, the disclosure or definition herein shall be deemed to prevail. –

Please replace paragraph 00102 on page 15 with the following amended paragraph:

-- For examples of the ~~difficultly~~ difficulty of performing HDA reactions using simple ketones, compare *inter alia*: (a) Guay, V.; Brassard, P. *Tetrahedron*, **1984**, *40*, 5039. (b) Schiess, P.; Eberle, M.; Huys-Francotte, M.; Wirz, J. *Tetrahedron Lett.*, **1984**, *25*, 2201. (c) Midland, M. M.; Graham, R. S. *J. Am. Chem. Soc.*, **1984**, *106*, 4294. (d) Daniewski, W. M.; Kubak, E.; Jurczak, J. *J. Org. Chem.*, **1985**, *50*, 3963. (e) Rigby, J. H.; Wilson, J. A. Z. *J. Org. Chem.*, **1987**, *52*, 34. (f) Chino, K.; Takata, T.; Endo, T. *Synth. Commun.*, **1996**, *26*, 2145. (g) Brouard, C.; Pornet, J.; Miginiac, L. *Synth. Commun.*, **1994**, *24*, 3047; (h) Huang, Y.; Rawal, V. H. *Org. Lett.*, **2000**, *2*, 3321. --

Please replace paragraph 00109 bridging pages 16 and 17 with the following amended paragraph:

-- Surprisingly and unexpectedly, the catalytic effect provided by hydrogen-bond donors can be extended to asymmetric or enantioselective synthesis. Throughout this

description and in the appended claims, the terms "asymmetric" and "enantioselective" are used interchangeably. Presently preferred chemical reactions that may be used in accordance with the present invention are reactions in which chiral hydrogen-bond donors can produce products having an excess of one enantiomer in relation to the other possible enantiomer. Representative chemical reactions include but are not limited to: Diels-Alder reactions, dipolar cycloadditions, carbene additions, cyclopropanation, aziridination, additions of nucleophiles to carbonyl groups (e.g., by Grignard reagents, stannanes, silanes, organozincs, and other organometallics), addition of nucleophiles to [[alpha, beta unsaturated]] alpha, beta-unsaturated carbonyls (e.g., by Grignard reagents, stannanes, silanes, organozincs, cuprates, organomanganese compounds, and other organometallics), nucleophilic addition to imines, cyanohydrin formation, cyanoamine formation, reductions of ketones and imines, and the like. --

Please replace paragraph 00129 on page 25 with the following amended paragraph:

Two additional TADDOLs, as shown in Scheme 10 below, were purchased from Aldrich Chemical Co. (Milwaukee, WI) and used to catalyze the HDA reaction between [[9]] 1 and **249**. 2-Naphthyl TADDOL **380** resulted in more undesirable products being formed than with TADDOL **379**. A NMR calculated yield for the reaction was ~30%. However, the product had an enantiomeric excess of 68%, demonstrating the significant enantioselectivity of the reaction. Surprisingly and unexpectedly, 1-naphthyl TADDOL **381** afforded a very clean reaction with few side products and the desired cycloadduct product was isolated in 63% yield. Remarkably, the ee of the cycloadduct approached nearly 100%, giving a greater than 200:1 enantiomeric ratio in the chiral HPLC spectrum. --

Please replace paragraph 00142 on page 30 with the following amended paragraph:

-- It should be noted that while 1-amino-3-siloxybutadiene **1** is a presently preferred diene for use in accordance with the present invention, other less electron rich

dienes, such as 1-amino dienes, also have ~~also~~ been used and shown to work. Examples of the reaction between a ~~[[1-amino- diene]]~~ 1-amino-diene with acroleins are shown in Table 6 below. --

Please replace paragraph 00143 on page 31 with the following amended paragraph:

– In view of the very promising results of the 1-naphthyl TADDOL-catalyzed ~~HDA~~ Diels-Alder reaction of aminosiloxy diene **505**, it is of interest to understand the mechanism and reactivity profile of this novel process. The gross structural features of the TADDOL class of ligands have been studied. At present, there are over 50 X-ray crystal structures of TADDOLs with a hydrogen bond acceptor (typically simple aliphatic alcohols, such as MeOH). All of the TADDOLs display C₂ symmetry with a propeller-type arrangement of the aryl rings. Unfortunately, there are no X-ray crystal structures of TADDOLs with an aldehyde. Results to date have suggested that the solvent plays an important role in the actual crystallization of the complex. --